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The Adsorption of Radionuclides on Bitumen

Part II: Nickel

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Abstract

The adsorption of $^{63}Ni^{2+}$ on a pure bitumen (Mexphalt 80/100) was studied as function of pH and ionic strength of the liquid phase. It was found that Ni^{2+} adsorbs on the bitumen surface by an inner sphere surface complexation reaction. The concentration ratio increases with increasing pH and ionic strength. At high pH values, the formation of neutral and anionic hydroxocomplexes in solution competes strongly with the adsorption reaction.

In a cementitious environment, the adsorption of Ni^{2+} on bitumen is negligible due to the formation of such hydroxocomplexes.

A theoretical evaluation of the adsorption of Am^{3+} and UO_2^{2+} on bitumen is given. These elements are expected to behave similarly to Ni^{2+}, i.e. an increase of R_a as a function of pH in the lower pH range, followed by a decrease due to the formation of hydroxocomplexes in the higher pH range.

Introduction

The adsorption of radionuclides on the bitumen matrix could be an important process retarding the release of radionuclides from the near field of a radioactive waste repository. The adsorption of radionuclides on bitumen has been studied previously [2–4] and it appears that the interaction of radionuclides with the bitumen surface is weak. Little information is available on the mechanisms of adsorption on bitumen and knowledge of the relevant parameters controlling the sorption process(es) is poor. In a previous study [1], the bitumen surface was characterized in terms of the functional group density (N_s, groups/cm^2). The adsorption of Sr^{2+} was measured under a variety of conditions and the results interpreted in terms of the formation of monodendate surface complexes.

In this work, the adsorption of Ni^{2+} on bitumen was studied. A mechanistic model was developed to describe the adsorption of Ni^{2+} as a function of pH, ionic strength and in the presence of competing ligands.

Materials and methods

Bitumen emulsions were prepared and characterized as described elsewhere [1]. The emulsions were placed in dialysis membranes (Dialysis Tubing-Visking, Medicell London) and equilibrated with solutions of the desired ionic strength and pH. Between pH 7 and 9, the solutions were buffered with $5 \cdot 10^{-4}$ M TRIS (Tris(hydroxymethyl)-aminomethane). Beyond pH 9, the pH was adjusted to the desired value by NaOH. The ionic strength of the solutions was fixed at 0.001 M with $NaClO_4$. In another series of experiments, the pH of the solutions was fixed at a value of 8.3 and the ionic strength was varied between 10^{-3} M and 10^{-2} M with $NaClO_4$. 20 ml aliquots of the bitumen emulsion were transferred to 50 ml teflon centrifuge (Oak Ridge Type) tubes and 5 ml of the equilibrium solution, spiked with $^{63}Ni^{2+}$, were added. The final concentration of Ni^{2+} was 10^{-8} M.

The mixtures were shaken end-over-end for 24 hours and subsequently centrifuged at 11000 g (Heraeus Sepatech, Biofuge 17S) for 30 minutes. 2 ml of the clear supernatant were sampled and analyzed for ^{63}Ni by liquid scintillation counting (Packard, Tricarb 2250 CA) using Instagel (Packard) as the scintillation cocktail. The concentration ratio (R_a^{Ni}) was calculated from the difference in concentration before and after equilibrium.

Parallel blank tests (without bitumen) were carried out to check the adsorption on the vessel walls.

Results and discussion

Figure 1 displays the adsorption results (R_a^{Ni}, cm) as a function of pH. The distribution ratio is defined as:

$$R_a^{Ni} = \frac{\text{Ni adsorbed}}{\text{Ni in solution}} = \frac{\mu\text{mol Ni/cm}^2}{\mu\text{mol Ni/cm}^3}. \quad (1)$$

As can be seen, the experimental data exhibit a relatively large scatter. Despite this, some clear trends can be identified. There is a sharp increase in adsorption with increasing pH in the pH range 7–8.5. Beyond pH 11, no, or very low, adsorption occurs. The increase in adsorption can be explained by an increase in the adsorption capacity (CEC) on the bitumen surface. The low adsorption at pH values >10.5 can be explained by the hydrolysis of Ni^{2+}. The formation of neutral $Ni(OH)_2^0$ or anionic $Ni(OH)_3^-$ and $Ni(OH)_4^{2-}$ species in solution competes with the adsorption of Ni^{2+} on the solid phase and makes adsorption impossible at higher pH values. As Ni^{2+} forms relatively stable complexes with i.a. carboxyl groups because of

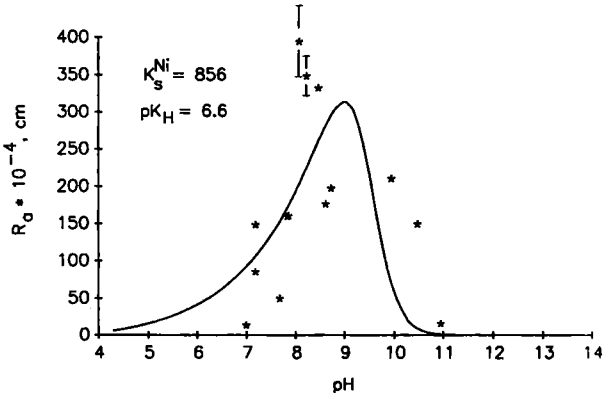

Fig. 1. Adsorption of Ni^{2+} on bitumen as a function of pH at I = 0.001 M. *: experimental results; —: calculated from equation (12).

its partly unfilled *d*-orbitals, the adsorption of Ni^{2+} was assumed to be a surface complexation reaction:

$$Ni^{2+} + RCOO^- \rightleftharpoons RCOONi^+. \quad (2)$$

The equilibrium constant is defined by:

$$K_s^{Ni} = \frac{\{RCOONi^+\}}{\{RCOO^-\}[Ni^{2+}] \cdot \gamma_{Ni}} \quad (3)$$

with: $\{RCOONi^+\}$ = Ni^{2+} adsorbed on the bitumen (μmol/cm²)
$\{RCOO^-\}$ = free, deprotonated carboxyl groups (μmol/cm²)
$[Ni^{2+}]$ = concentration of Ni^{2+} in solution (μmol/cm³)
γ_{Ni} = activity coefficient of Ni^{2+} in solution.

In cases where complexation or hydrolysis reactions occur, these reactions have to be combined with the adsorption reaction.
The following reactions of Ni^{2+} occur in solution:

$$Ni^{2+} + L^{2-} \rightleftharpoons NiL \quad (4)$$

with

$$K_{NiL} = \frac{[NiL]}{[Ni^{2+}] \cdot [L^{2-}]} \quad (5)$$

and

$$Ni^{2+} + nOH^- \rightleftharpoons Ni(OH)_n^{2-n} \quad (6)$$

with

$$\beta_n = \frac{[Ni(OH)^{2-n}]}{[Ni^{2+}][OH^-]^n} \quad (7)$$

where $n = 1, 2, 3, 4$.
This gives:

$$[Ni]_{tot} = [Ni^{2+} + NiL + \sum_{n=1}^{4} Ni(OH)_n^{2-n}] = [Ni^{2+}]\left(1 + K_{NiL}[L^{2-}] + \sum_{n=1}^{4} \beta_n \cdot [OH^-]^n\right). \quad (8)$$

The combination of equations (3) and (8) results in:

$$K^{Ni}{}_s = \frac{\{RCOONi^+\}}{\{RCOO^-\} \cdot [Ni]_{tot} \cdot \gamma_{Ni}/(1 + K_{NiL}[L^{2-}] + \sum_{n=1}^{4} \beta_n[OH^-]^n)} \quad (9)$$

Since we are studying the adsorption of Ni^{2+} at trace levels, the adsorption of Ni^{2+} on the surface does not change the composition of the surface significantly. Consequently, the activity coefficient of the adsorbed species can be considered to be constant and is included in the equilibrium constant. The deprotonation of the carboxyl groups is controlled completely by the Na^+ concentration in and the pH of the liquid phase. With $\{RCOONi^+\}/[Ni]_{tot} = R_a^{Ni}$ and $\{RCOO^-\}$ = CEC, equation (9) is transformed in:

$$K_s^{Ni} = \frac{R_a^{Ni}}{CEC \cdot \gamma_{Ni}/(1 + K_{NiL}[L^{2-}] + \sum_{n=1}^{4} \beta_n[OH^-]^n)} \quad (10)$$

or

$$R_a^{Ni} = \frac{K_s^{Ni} \cdot CEC \cdot \gamma_{Ni}}{1 + K_{NiL}[L^{2-}] + \sum_{n=1}^{4} \beta_n[OH^-]^n} \quad (11)$$

and with $CEC = \alpha \cdot CEC_{max}$,

$$R_a^{Ni} = \frac{K_s^{Ni} \cdot \alpha \cdot CEC_{max} \cdot \gamma_{Ni}}{(1 + K_{NiL}[L^{2-}] + \sum_{n=1}^{4} \beta_n[OH^-]^n)} \quad (12)$$

R_a^{Ni} = concentration ratio of Ni (cm)
K_s^{Ni} = surface complexation constant (cm³/μeq)
CEC_{max} = maximal CEC (μeq/cm²)
K_{NiL} = stability constant of the NiL complex (M^{-1})
β_n = hydrolysis constant of $Ni(OH)_n^{2-n}$
$[L^{2-}]$ = concentration of ligand L in solution (M)
$[OH^-]$ = concentration of OH^- in solution (M).

Equation (12) is the basic equation describing the adsorption of Ni^{2+} on bitumen as a function of pH and the concentration of competing ligands L and OH^- in solution. $K_{NiL} \cdot [L^{2-}]$ in equation (12) can be set to zero, since no complex forming organic or inorganic ligands other than OH^- were present. The CEC equals the amount of dissociated carboxyl groups on the surface and can be calculated from the Ionizable Surface Group Model with $pK_H = 6.6$ and $CEC_{max} = 2.28$ μeq/m² [1].

The solid line in Figure 1 shows a least square fit of the sorption data derived from equation (12). The parameter used for the fit are summarized in Table 1. The surface complexation constant was derived from this least square fit and equals 856 ± 122. All other parameters were fixed. The calculated curve describes

Table 1. Parameter values used in equation (12) to describe the adsorption of Ni^{2+} on bitumen

Parameter	Value
pK_H**	6.6
K_s^{Ni}	856
CEC_{max}**	2.28
$[Na^+]$	0.001 M
β_1*	$10^{4.27}$
β_2*	$10^{8.0}$
β_3*	10^{12}
β_4*	10^{12}

* Taken from [8].
** Taken from [1].

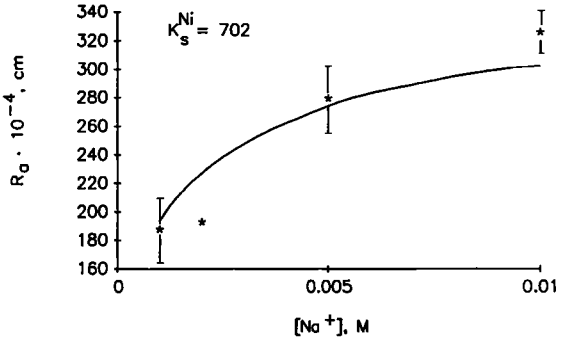

Fig. 2. Adsorption of Ni^{2+} on bitumen as a function of the Na^+ concentration at pH = 8.3. *: experimental results; —: calculated from equation (12).

Table 2. Stability constants of complexes between M and acetate [6]

Metal	$\log K_1$	K_1
Sr^{2+}	1.19 (I = 0, 25°C)	15.5
Ni^{2+}	1.43 (I = 0, 25°C)	26.2
Am^{3+}	2.78 (I = 0, 20°C)	602
UO_2^{2+}	3.03 (I = 0, 20°C)	1071

reasonably the increase of R_a^{Ni} in the pH range 7–9, the maximum at a pH of 9.2 and the decrease in R_a^{Ni} at pH > 9.2. At pH values > 11, the adsorption of Ni^{2+} is negligibly small.

Figure 2 shows the adsorption of $^{63}Ni^{2+}$ (R_a^{Ni}) as a function of the Na^+ concentration in the liquid phase at a constant pH of 8.3. The higher the Na^+ concentration, the higher the adsorption of Ni^{2+}. According to the Ionizable Surface Group model, the deprotonation of the surface carboxyl groups depends strongly on the ionic strength of the liquid phase in the pH range 6–11 [1]. The adsorption capacity (CEC) thus increases with increasing ionic strength. When the ionic strength is raised from 0.001 M to

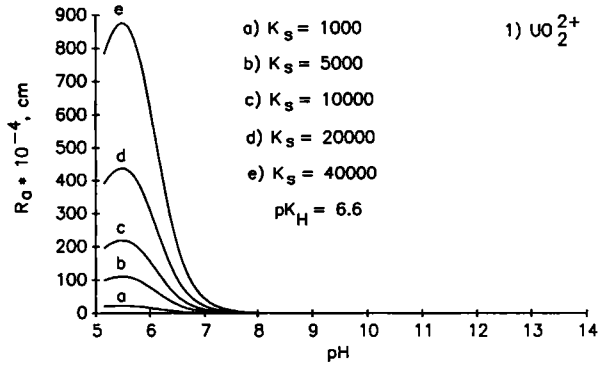

Fig. 3. Adsorption of UO_2^{2+} on bitumen as a function of pH at I = 0.001 M as calculated from equation (12).

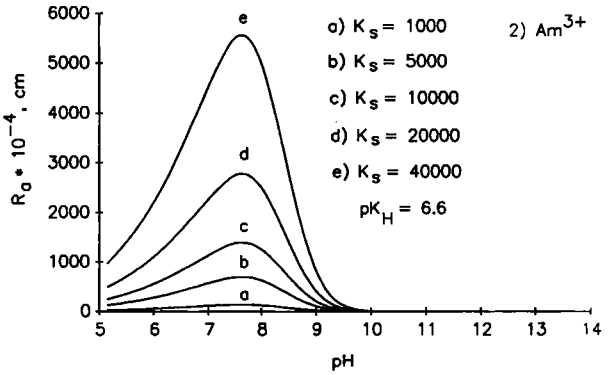

Fig. 4. Adsorption of Am^{3+} on bitumen as a function of pH at I = 0.001 M as calculated from equation (12).

0.01 M at pH 8.3, the value of α increases from 0.15 to 0.29. The CEC ($CEC = CEC_{max} \cdot \alpha$) thus increases by a factor 2 from 0.34 to 0.66 μeq/m² [1]. Consequently, the distribution ratio increases with a factor two by raising the ionic strength from 0.001 M to 0.01 M at a constant pH of 8.3. The solid line in Figure 2 represents the evolution of R_a^{Ni} as a function of the Na^+ concentration as calculated by equation (12). The experimental and predicted values are in good agreement. The value of K_s^{Ni} derived from this least square fit equals 702 ± 35 and is similar to the value derived earlier.

The surface complexation reaction (interaction of a surface carboxyl groups with Ni^{2+}) is independent on the Na^+ concentration in solution. Consequently, this reaction can be assumed to be an inner sphere surface complexation reaction. Inner sphere complexes result from the formation of a covalent bond between the coordinating atoms and the metal ions, with partial or total dehydration [5]. The Ni^{2+} ion is thus located in the Stern layer and not in the diffuse part of the double layer. The distribution ratio, however, depends on the ionic strength because the CEC depends on the ionic strength.

Equation (12) allows us to evaluate the adsorption of Ni^{2+} on bitumen under the near field conditions of a cement based repository [7]. At these high pH values,

Table 3. Parameter values used in equation (12) to calculate adsorption of Am^{3+} and UO_2^{2+} on bitumen

Parameter	Value	Species
pK_H**	6.6	–
CEC_{max}**	2.28	–
$[Na^+]$	0.001 M	–
$\log\beta_1$*	6.0	$Am(OH)^{2+}$
$\log\beta_2$*	11.10	$Am(OH)^+$
$\log\beta_3$*	15.50	$Am(OH)_3^0$
$\log\beta_4$*	18.90	$Am(OH)_4^-$
$\log\beta_1$*	8.20	$UO_2(OH)^+$
$\log\beta_2$*	16.0	$UO_2(OH)_2^0$
$\log\beta_3$*	18.4	$UO_2(OH)_3^-$
$\log\beta_4$*	18.20	$UO_2(OH)^{2-}$

* Taken from [9].
** Taken from [1].

Ni^{2+} is completely hydrolysed ($Ni(OH)_3^-$: 72%; $Ni(OH)_4^{2-}$: 28% [8]) and adsorption on bitumen is negligibly small. The R_a^{Ni} values can be estimated to be $<10^{-6}$ cm.

Equation (12) can also be used to evaluate the adsorption of other cationic radionuclides on bitumen. Let us consider the adsorption of uranium and americium under oxic conditions. Under these conditions, U(VI) and Am(III) are predominant. As no information is available on the surface complexation constants K_s^{Am} and $K_s^{UO_2}$ on bitumen, reasonable estimations have to be made.

To facilitate this estimation, comparison with stability constants of metal-acetate complexes in solution were made [6]. Table 2 gives an overview of stability constants of a few 1:1 metal-acetate complexes. The stability constant of Ni^{2+} is about 2 times higher than that for Sr^{2+}. The Am^{3+} and UO_2^{2+} constants are 23 and 41 times higher than the Ni^{2+} constants. Taking the surface complexation constant for Ni^{2+} as a reference and assuming a constant ratio between surface COOH and solution acetate constants, one can calculate surface complexation constants of 20000 (Am^{3+}) and 35000 (UO_2^{2+}) as reasonable estimates.

Figures 3 and 4 display the R_a for UO_2^{2+} and Am^{3+} as a function of pH. The values of K_s^{Am} and $K_s^{UO_2}$ were varied, for illustration, between 1000 and 40000. The values of the other parameters used for the calculations are given in Table 3. It is assumed, for simplicity, that only the hydrated cation is adsorbed on the bitumen surface. This is probably an oversimplification of the adsorption process but, nevertheless, enables realistic estimations of the extend of adsorption on the bitumen surface to be made.

The same observations can be made as for Ni^{2+}. Adsorption (R_a) increases as a function of pH, reaches a maximum and decreases again at higher pH values. The pH at which a maximum occurs depends on the values of the hydrolysis constants. The higher the tendency of an ion to undergo hydrolysis, the lower the pH at which an adsorption maximum occurs. The hydrolysis constants of Am^{3+} and UO_2^{2+} found in the literature exhibit a relatively large uncertainty but this has, however, no influence on the conclusions which can be drawn from the calculations. At pH values typical of a cementitious environment (pH = 12–13), adsorption of both Am^{3+} and UO_2^{2+} is expected to be negligible due to complete hydrolysis.

For cationic hydrolyzable radionuclides present in the waste matrix, one can conclude, in general, that no or very weak adsorption on bitumen has to be expected in a cementitious environment.

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